

IONIC LIQUIDS FOR ADVANCED MATERIALS

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ABSTRACT

Multidisciplinary research has served as the cornerstone of the first year ILEAD MURI programs leading to working collaborations among scientists and engineers with graduate student exchanges, real-time feedback, and multidisciplinary peer-reviewed publications. The MURI research team is organized according to interdisciplinary and integrative fundamental questions of science and engineering, and these grand challenges serve to assemble researchers from diverse disciplines. Unprecedented charged polymer compositions have been prepared with attention to the correlation of charge density and chemical composition with morphological structure in the both the solution and solid state. Scattering studies have revealed the importance of charge location on structure at the nanoscale and the correlation of structure with membrane performance. Novel families of electromechanical transducers were discovered with special attention to the design of assembled structures based on the tuning of electrostatic interactions. These novel transducers have demonstrated unparalleled performance. The MURI team has developed characterization set-ups for the electromechanical responses of conductive network/ionomer composite (CNIC). The overall research goal is to develop a micromechanical model for the electrochemomechanical transduction mechanisms in newly synthesized ionic liquid polymers in order to predict optimal material properties which can be used for ionic liquid and polymer synthesis.

INTRODUCTION

The ILEAD MURI research program involves an integrated and interdisciplinary strategy for the discovery of both low molar mass IL solvents and high molar mass polymers containing novel charged monomers based on IL building blocks. Our overarching scientific objective is the fundamental correlation of macromolecular chemistry and architecture with fundamental physical properties and device performance. Areas of potential Army impact range broadly from electromechanical transducers and electrochromic devices to selective membranes for chemical and biological protection and fuel cells.

ILs have moved from simple laboratory curiosities to industrial products and processes. ILs do not obey typical relationships that simply correlate an increase in the glass transition temperature (T_g) with an increase in dielectric constant and ion content. ILs uniquely combine high dielectric constant, low volatility, high free ion content, large electrochemical window, and low T_g to enable the design of polymeric materials for a wide variety of electronic and transport devices. Thus, a fundamental understanding of ILs offers a unique opportunity to significantly improve the performance of various electro-active devices for Army applications. The presentation will focus on critical applications for IL-containing polymeric materials with a keen awareness of fundamental questions and the discovery of a new “toolbox” of IL building blocks and complementary characterization tools.

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Solid-state electromechanical actuators (EMAs) with large strain, high elastic energy density, and low operation voltage are in great demand for DoD applications such as MEMS, large-scale tunable antennas, smart materials and systems, morphing aircraft skin, and energy harvesting. Traditional inorganic EMAs such as the piezoceramic PZTs suffer from very low actuation strain ($\sim 0.1\%$) and high operation voltage (>300 volts). Among various EMAs, ionic electroactive polymers (*i*-EAPs) are extremely attractive because only a few volts are required for actuation. As will be described in the presentation, both experimental results and molecular considerations indicate the potential of novel IL-containing polymers and nanostructures for achieving high electromechanical responses with significantly improved response speed, strain level and elastic energy density, efficiency, and wide operational temperature range.

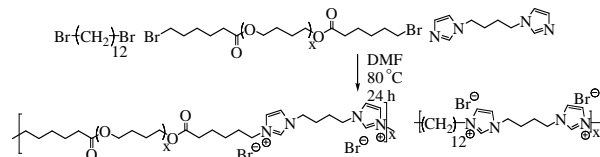
IL-containing high performance membranes are suitable for a number of applications, including fuel cells, batteries, actuators, sensors, water purification, pervaporation, and selective barriers. These applications require high flux of the desired diffusant and high selectivity (low flux of the undesired diffusant). For example, lightweight and breathable barriers are the central element for chemical and biological protective clothing for soldiers as an alternative to the JSLIST suit (Joint Service Lightweight Integrated Suit Technology, current standard used by the US armed forces). The JSLIST only has a selectivity of only ~ 2 (water/toxin transport) and has a limited protection time. Furthermore, the methanol fuel cell currently operates at only 20% efficiency due to low membrane selectivity (proton/methanol transport). ILs, IL-inspired polymers, and charged polymers swollen with ILs provide new opportunities to design highly permselective membranes.

IONENES

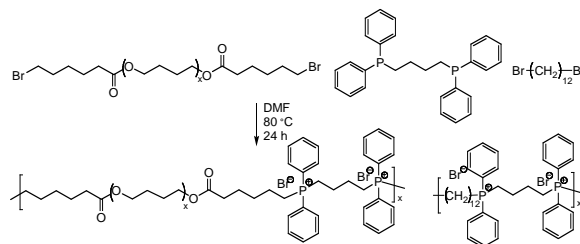
Ammonium polyionenes, or ionenes, are ion-containing polymers that contain quaternary nitrogen atoms in the macromolecular backbone of the repeating unit, as opposed to a pendant position. Ionene synthesis occurs via a step-growth polymerization of a dialkyl halide and a ditertiary amine in a Menshutkin reaction. The aim of this part of the project is to synthesize and characterize the mechanical properties of novel ionenes. Water-soluble 12,12-ammonium ionenes were prepared via the Menshutkin reaction, and a stoichiometric imbalance of monomers controlled the final molecular weights of the polymers. Relationships between weight-average molecular weight and mechanical properties were established for a series of 12,12-ammonium ionenes using both tensile testing and

dynamic mechanical analysis (DMA). Tensile analysis of the higher molecular weight ionenes revealed an average tensile strength of 20 MPa and elongations ranging from 230-440%. Dissociation of ionic aggregates was observed at 85-88 °C in DMA experiments, and the glass transition temperatures increased with increasing molecular weight (61-88 °C). X-ray scattering (in collaboration with the Winey group) revealed an amorphous polyethylene peak at approximately 14 nm⁻¹ and a sharp ionic group correlation peak at 4.38 nm⁻¹. These correlations agreed well with the proposed macromolecular structure.

To investigate the influence of hard segment content on thermal and mechanical performance, a series of novel imidazolium and phosphonium ionenes were synthesized with increasing amounts of hard segment incorporated through the use of 1,12-dibromododecane (**Schemes 1 and 2**).



Scheme 1. Synthesis of imidazolium ionenes containing PTMO and short aliphatic segments.



Scheme 2. Synthesis of phosphonium ionenes containing PTMO and short aliphatic segments.

A fundamental investigation of the influence of phosphonium and imidazolium bromide salts within the polymer main chain of polyurethanes was conducted to elucidate the effect of ionic associations on hard segment hydrogen bonding. Differential scanning calorimetry (DSC) revealed that phosphonium polyurethanes were relatively more crystalline compared to non-charged analogs, and it was presumed that enhanced hydrogen bonding in the non-charged polyurethanes restricted polymer mobility and reduced PTMO crystallinity. Moreover, FT-IR spectroscopy demonstrated that hydrogen bonding interactions were significantly reduced in the presence of phosphonium cations. These results correlated well with tensile properties, i.e., the non-charged polyurethanes offered both superior tensile strengths and elongation values

compared to phosphonium polyurethanes. Wide-angle X-ray scattering (WAXS) data indicated that both the phosphonium polyurethane and the non-charged polyurethane were amorphous at ambient temperature, and small-angle X-ray scattering (SAXS) indicated that the polyurethanes exhibited hard segment microphase separation. Scanning transmission electron microscopy (STEM) of phosphonium polyurethanes revealed ion-rich domains within the hard segments and energy-dispersive X-ray spectroscopy (EDS) during STEM imaging confirmed the elemental composition of the ionic aggregates. Ion-containing polyurethanes containing bisimidazolium functionality in the hard segment also possess unique thermomechanical, tensile, and morphological behavior. Specifically, influences of imidazolium-containing polyurethanes on TGA, DSC, DMA, FT-IR, X-ray scattering, STEM, and EDS results were observed. Both polyurethanes do not dissolve in ionic liquids and show promise as novel polymers for transducer applications.

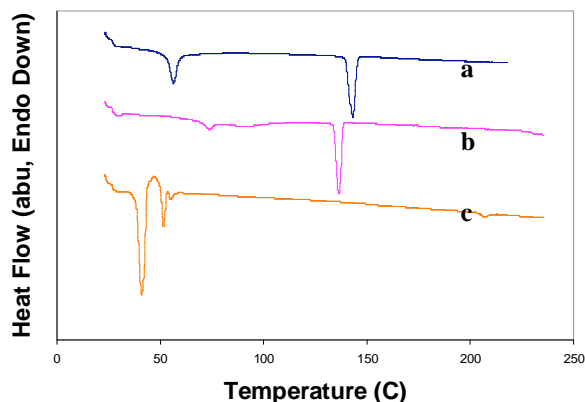
IMIDAZOLIUM-BASED GEMINI SURFACTANTS

Amphiphilic monomers provide the ability to aggregate into preferred structures based on solution and thermal conditions. Examples of such structures include the lipid bilayer cell membrane as well as the liquid crystalline assemblies within display screens. The imidazolium cation provides an ideal base for the design of amphiphilic monomers due to the ease of functionalization and ion exchange. In addition, hydrophilicity and thermal properties of imidazolium molecules will vary controllably over a significant range by simple changes in molecular and counteranion structure.

Imidazolium-based gemini surfactants were prepared with a short, rigid alkyl spacer and long alkyl chains. Gemini surfactants comprise two hydrophilic headgroups connected by a rigid spacer, with a long hydrophobic group attached to each headgroup. The term *m-n-m* will be used to refer to gemini surfactants with alkyl chains of *m* carbons as the long tails and a rigid alkyl spacer of *n* carbons. Surfactants 12-2-12 and 16-2-16 were prepared with bromide counterions, and the thermal properties analyzed in depth. Two endothermic transitions were observed upon heating, one between 50 and 70 °C, and the second transition around 150 °C. Based on comparison to a previously reported 16-1 monomeric imidazolium based surfactant, the lower temperature transitions are believed to be crystalline to liquid crystalline phase transitions, and the upper transition is believed to be melting into an

isotropic phase. Figure 1 shows the DSC thermograms of each surfactant as well as the 16-1 comparison. Experiments are ongoing to confirm the existence of a liquid-crystalline phase. The presence of such an ordered phase could apply these imidazolium systems to applications including ion/electron transport and molecularly-selective separations.

Figure 1. DSC thermograms of gemini surfactants a)



12-2-12 b) 16-2-16 c) 16-1.

Preliminary experiments also indicate that changes in molecular structure can affect the gemini surfactants' melting transition. After exchanging the bromide anions for tetrafluoroborate, the melting point decreased by approximately 20 °C. Similarly, increasing the length of the rigid spacer from two carbons to four or six carbons decreased the melting transition by 50 and 70 °C, respectively. Both adjustments showed little effect on the lower temperature transition. Addition future work includes synthesis of monomers based on the gemini surfactants and studying the polymer properties of such amphiphilic properties.

In addition, to study the effect of counteranion and polyelectrolyte hydrophobicity on solution rheology and electrospinning characteristics, polyelectrolytes based on the monomer 2-(N,N-dimethylamino)ethyl methacrylate were synthesized with varying counteranions (chloride and tetrafluoroborate). Preliminary experiments indicate that counteranion has a significant effect on the rheology and electrospinning behavior. The plot in figure 2 shows the preliminary rheology of the uncharged polymer (PDMAEMA), and the protonated polymer with chloride and tetrafluoroborate counteranions (PDMAEMA-HCl and PDMAEMA-HBF₄, respectively).

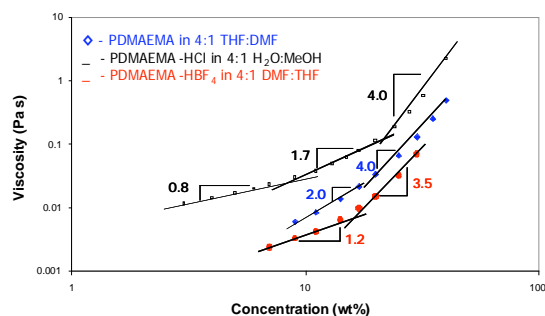


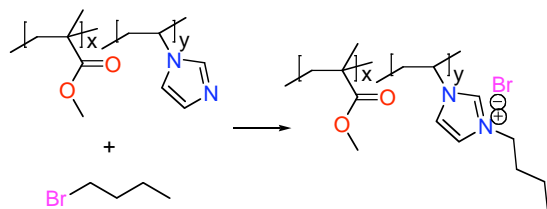
Figure 2. Rheology of PDMAEMA in various solvents and conditions.

PDMAEMA shows typical behavior of a polymer in theta solvent, which is reasonable for this polymer in a THF:DMF mixture. Once titrated with HCl, however, the PDMAEMA-HCl shows strong polyelectrolyte behavior in aqueous solution. When the counteranion is exchanged to the hydrophobic tetrafluoroborate, the polymer behavior appears to become an average of polyelectrolyte and neutral polymer behavior. More controlled experiments are underway. In addition, preliminary electrospinning experiments indicate that PDMAEMA exhibits neutral polymer behavior during electrospinning (onset concentration for fiber formation $\sim C_e$). The polyelectrolytes, however, demonstrate significant differences, especially in the onset concentration for fiber formation. Both PDMAEMA-HCl and PDMAEMA-HBF₄ require concentrations almost four times the C_e before fibers will form during electrospinning, a characteristic of polyelectrolyte behavior. More experiments investigating the electrospinning behavior of these polyelectrolytes are ongoing.

IONIC LIQUID CONTAINING POLYMERS

Ionic liquids possess a variety of favorable characteristics including high thermal stability, reasonable ionic conductivity, nonvolatility and even anti-microbial behavior. Ionic liquid-containing (co)polymers represent a unique class of polyelectrolytes since they have relatively high thermal stability and offer high ionic conductivity. Additionally, chemo/physical characteristics of the polymer can be easily tuned by exchanging the counterion on the polymer/monomer. These properties make ionic liquid-containing polymers suitable candidates for materials in energy storage devices, such as batteries and fuel cells, and electromechanical actuators. We have synthesized ionic liquid-based polymers using 1-vinylimidazole precursors. Additionally, we evaluated the swellability of the synthesized ionic liquid-containing polymer films with small molecule diluents, such as water and low molecular weight ionic liquids.

We synthesized a series of 1-vinylimidazole (VIM), methyl methacrylate (MMA) random copolymers via conventional free radical polymerization in solution. The synthesized copolymers had VIM content ranging from 5-80 mol% as measured using ¹H NMR spectroscopy. Once synthesized, the copolymers were alkylated with 1-bromobutane to convert the imidazole groups into imidazolium bromide, see Scheme 3 below.



Scheme 3. Alkylation of VIM, MMA copolymers.

Films of the MMA-VIM were prepared by solution casting in Teflon molds (Figure 3). Once prepared, the free-standing films were extraordinarily brittle. To improve ductility, the films were immersed in 1-ethyl-3-methylimidazolium methyl sulfate, a low MW ionic liquid (Figure 4). However, it was observed that the films completely dissolved in the low MW ionic liquid (Figure 5). Ionic conductivity measurements were performed with samples having 50 mol% vinylimidazolium bromide groups. These experiments found that the bulk ionic conductivity of films prepared from this sample was roughly 10^{-9} S/cm at room temperature and ambient humidity.



Figure 3. Poly(methyl methacrylate-co-1-butyl-3-vinylimidazolium bromide) (50mol% MMA) film solution cast from ethanol.

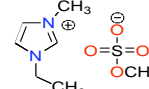


Figure 4. Chemical structure of 1-ethyl-3-methylimidazolium methyl sulfate ionic liquid.



Figure 5. Poly(methyl methacrylate-co-1-butyl-3-vinylimidazolium bromide) (50mol% MMA) film dissolving in ionic liquid.

To prevent dissolution of ionic liquid-containing polymer films in low MW ionic liquids, we synthesized ionic liquid monomer-based crosslinked gels. We first synthesized an ionic liquid-based monomer (1-butyl-3-vinylimidazolium bromide, BVIM) as shown in Figure 6 (Amajjahe et al., 2008).

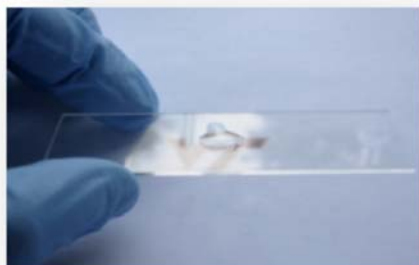
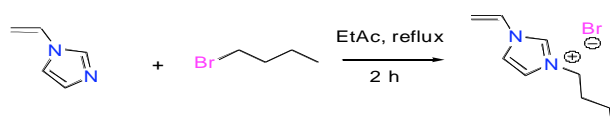
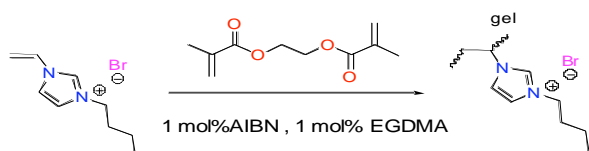


Figure 6. Synthesis of BVIM.



Scheme 4. Synthesis of BVIM-based gels using EGDMA as a tetrafunctional crosslinking agent.

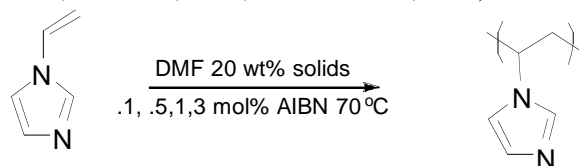
Crosslinked films were prepared by the reaction of BVIM and ethylene glycol dimethacrylate (EGDMA) shown in scheme 4. Various films were prepared using different levels of EGDMA and AIBN to achieve free standing films, shown in Figure 7. The crosslinked films were insoluble in organic solvent, water, and low MW ionic liquids.



Figure 7. Photograph of BVIM-gel hydrated with humid air.

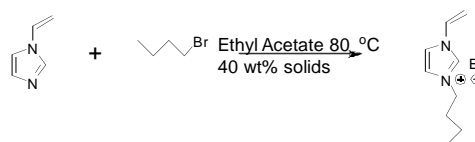
Imidazole-containing polymers represent a relatively unexplored field in terms of modern chemistry. The tertiary nitrogen in the imidazole ring is easily protonatable by either an acidic environment or

substitution which results in a cationic quaternary nitrogen atom. In several cases, substitution resulting in quaternary nitrogen atoms results in ionic liquid properties. Imidazole containing polymers are used in a variety of applications including ester hydrolysis catalysts, non-viral gene delivery vectors, and formation of catalysts via coordination complex formation with transition metals (Overberger et al., 1963; Ihm et al., 2005; Muldoon et al., 2004).



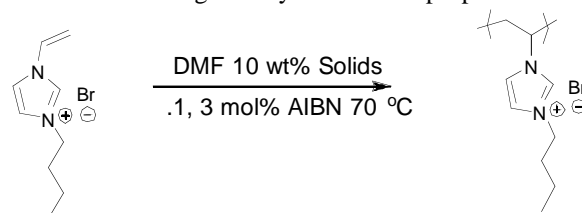
Scheme 5. Synthesis of pVIM.

A homopolymer of poly(1-vinylimidazole) (pVIM) is synthesized using free radical initiator (AIBN) at 70 °C overnight (Scheme 5). While this particular polymer does not possess properties which can be utilized for electroactive devices, knowledge gained of free-radical polymerization will be beneficial for synthesis of ionic polymers. The resulting polymer has a thermal stability and properties characteristic of imidazole-containing molecules. The onset of degradation occurs around 375 °C and the glass-transition temperature is 175 °C.



Scheme 6. Synthesis of BVIM.

The ionic liquid monomer, 1-butyl-3-vinylimidazolium bromide (BVIM) is synthesized by alkylation of 1-vinylimidazole (VIM) in refluxing ethyl acetate (Scheme 6). The resulting ionic liquid is extremely viscous, and requires further thermal and mechanical testing to fully evaluate its properties.



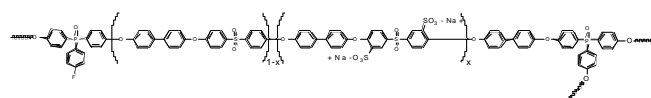
Scheme 7. Synthesis of pBVIM.

The ionic liquid monomer can be polymerized to form poly(1-butyl-3-vinylimidazolium bromide) (pBVIM) using AIBN to initiate a reaction (Scheme 7). The mechanical and thermal properties of this polymer are forthcoming. Exchanging the anion (bromide) with tetrafluoroborate will allow for evaluation of the effect that the counterion has on the molecule and its properties. Evaluation of the mechanical and thermal

properties of all of these molecules will provide insight into further developing electroactive devices derived from ion-containing polymers.

THE INFLUENCE OF CONTROLLED BRANCHING IN POLYSULFONE IONOMERS FOR APPLICATIONS IN IONIC LIQUID SWOLLEN TRANSDUCERS

The effect of branching on the morphology, physical properties, and electromechanical transduction of polysulfone ionomers is under investigation. These studies aim to better understand the relationship established between polymer topology and ionic polymer transducer performance (swollen with ionic liquids) as electromechanical sensors and actuators. The process of tuning novel synthetic polymers for application as ionic polymer transducers (IPT) requires attention to the interface of all components of the composite device. Our recent work concentrates on the interface of the ionomer with the conductive particles in the electrode as well as the interface of the polymer membrane with the ionic liquid diluent. The latter case has bearing on the performance of the central membrane in charge transport in addition to the formation of the matrix morphology supporting the conductive particles in the electrodes. A branched polysulfone with 20 mol % sulfonate functionality (HB-3kBPS-20, Scheme 1) was both swollen and separately cast in the presence of various uptakes of a hydrophilic ionic liquid. Due to the high dielectric constant of the ionic liquid, increases in its uptake within the polymer membrane serves to increase the inherent ionic conductivity of the device which typically leads to better transduction performance.



Scheme 9. Chemical structure for a highly branched sulfonated polysulfone.

To facilitate a proof of the original novel IPT concept, an ionomer membrane cast with an ionic liquid (EMI-Tf) uptake of 4.90 mol EMI-Tf/mol SO_3^- was used to construct the first IPT ever constructed from 100 % novel synthetic ionomers with the direct application process (DAP). The same ionomer was used in cast membranes containing RuO_2 conducting particles to form electrodes. These electrodes were melt-pressed on either side of the central IL-swollen membrane and further coated with a layer of gold leaf to form the fully assembled IPT (Figure 8). When placed in a cantilever configuration between two electrical leads, the application of a 1 V DC potential caused a bending actuation response. Subsequent efforts aimed to optimize the electrode composition and

ionomer-IL interface to achieve maximum ionic conductivity leading to increased strain during actuation.

Previous work in the literature demonstrated that loading of conducting particles in the IPT electrode above a percolation threshold increased ionic conductivity by three orders of magnitude. An investigation into the effects of varied loadings (0-45 vol %) of electrically conducting RuO_2 particles on impedance characteristics of IPT electrodes was therefore performed in an attempt to optimize the active layer for this novel transducer. Free-standing electrode layers were cast from homogeneous dispersions of RuO_2 , EMI-Tf, and HB-3kBPS-20. The loading of ionic liquid to HB-3kBPS-20 was kept constant at ~4.9 mol EMI-Tf/mol SO_3^- . Electrical impedance spectroscopy (EIS) was conducted on the cast electrodes with a through-thickness fixture to mimic the geometry used in IPT performance. A 100 mV rms applied potential produced the impedance response from 0.1 Hz – 15 MHz shown in the Bode plot in Figure 9.

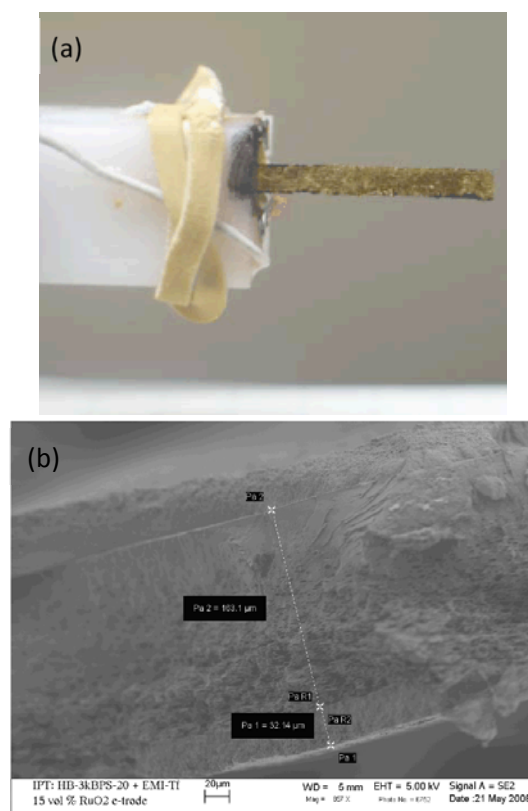


Figure 8 (a) IPT constructed from HB-3kBPS-20 / EMI-Tf / RuO_2 / gold leaf (b) SEM micrograph of the IPT cross-section with electrodes composed of EMI-Tf, RuO_2 (15 vol %), and HB3kBPS-20 (85 vol %)

The Bode plot in Figure 9 displays a direct trend of decreasing impedance magnitude with

increased loading of RuO₂ particles. For these stand-alone electrodes, increased loading up to 45 vol % RuO₂ decreased the low frequency impedance by approximately four orders of magnitude while the high frequency impedance decreased by nearly two and a half orders of magnitude. The other noticeable characteristic within this trend was that there appeared to be a large drop in impedance between 22.5 – 30 vol % RuO₂, implying a percolation threshold. Percolation leads to a characteristic pure conductor and is further supported by the phase data that shows an angle of zero degrees across the entire frequency range of interest for loadings of RuO₂ above 22.5 vol %. The corresponding series of IPTs built with analogous electrode loadings demonstrated similar percolation in bending strain with a maximum at 45 vol % RuO₂. Further, equivalent circuit modeling of the electrode percolation in impedance identified the interfacial resistance between the conducting particle and ionomer, not solely the ionic conductivity of the ionomer, as a main electrode parameter for tuning performance of IPTs.

Moving focus to the central membrane of the IPT, SEM revealed a processing artifact in the construction of the central ionomer membrane (Figure 8b). The membranes were cast from solution in the presence of the desired loading of ionic liquid. All SEM micrographs revealed a porosity gradient across the thickness of the membrane, suggesting that the ionic liquid did not remain homogeneously dispersed in the polymer solution during casting. Our hypothesis was further supported by the fact that the cast membranes displayed a transition from optical clarity to completely opacity with increased amounts of ionic liquid. This transition was not previously observed in Nafion[®] membranes swollen with the same ionic liquid. The observation required further investigation due to its implications for ionic conductivity and stability of the RuO₂/ionic liquid/polymer dispersion employed to create the electrodes with the direct application process (DAP).

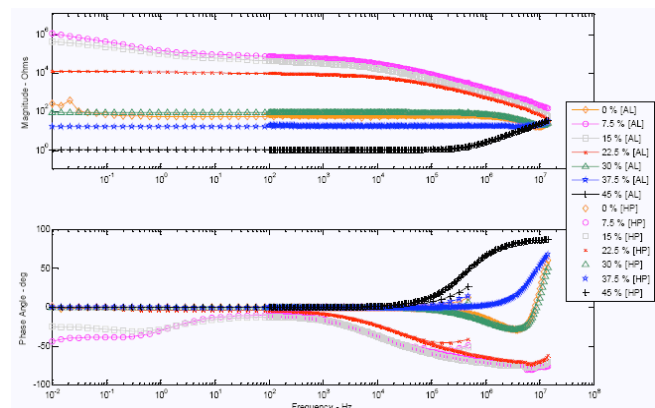


Figure 9. Bode plot for magnitude of the impedance and phase angle versus frequency for stand-alone IPT electrodes cast with varied volume percent of RuO₂

To probe the effects of casting membranes in the presence of ionic liquid, electrical impedance spectroscopy (EIS) was performed on a series of samples containing 0 – 100 wt % ionic liquid per weight of the polymer (HB3k-BPS-20, Figure 10). Hypothetically, the ionic liquid appears to have precipitated from the dimethylacetamide (DMAc) solution before the polymer approached high concentration and the solid state. The gradient also suggests that the ionic liquid settled to the bottom of the membrane during its formation. If so, this scenario implies that in-plane ionic conductivity is greater for the membrane face that was in contact with glass than the face open to the air and DMAc evaporation. The ionic conductivities derived from through-thickness and in-plane impedance measurements are provided in Figure 4. Figure 4 displays two main characteristics in the ionic conductivity of the membranes. First, conductivity is anisotropic between the Z and X dimensions of the membrane, where charge transport in the X direction is much greater than the Z direction. Second, casting in the presence of ionic liquid, as indicated by conductivity, does impose an inhomogeneous distribution in the Z direction. The in-plane conductivity of the membrane face formed at the glass is greater than that of the air-polymer interface for all uptake levels, and is accentuated at high uptakes. These trends imply that casting in the presence of ionic liquids increases the conductive anisotropy apparent in dry membranes and motivated us to explore other methods for incorporation of ionic liquid into the transducer.

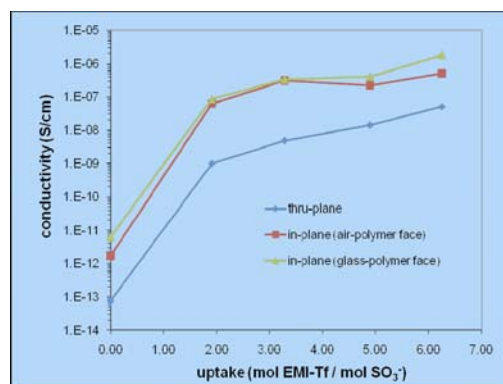


Figure 10. Ionic conductivity versus cast uptake of EMI-Tf in HB3k-BPS-20 membranes for in-plane measurements on both membrane faces and through-thickness geometry.

To advance toward the goal of increasing the overall ionic conductivity of the IPT, swelling studies for optimization of uptake were performed with variation in time, temperature, and identity of a co-diluent. Temperature was found to have the greatest effect on uptake magnitude. In comparison to the

samples cast in the presence of ionic liquid, the same membrane swollen instead provides similar or higher ionic conductivity values at lower levels of ionic liquid uptake. This trend was demonstrated for linear and branched samples, although conductivity trends were more dominated by the inherent degree of sulfonation. Characterization is presently under way to confirm the effect of these variables on the microphase separated morphology of the IPT membrane and the location of the ionic liquid during uptake. All cast and swollen samples were submitted for SAXS analysis to detect changes in the polymer morphology based on the presence, location, uptake level and method for incorporation of ionic liquid into the ionomer. Stability of the membrane's charge transport pathways is essential to operation as both a sensor and actuator.

The two main studies conducted during this period served to expand the DAP process to the use of novel ionomers, a first for IPTs. The use of EIS enabled correlation of physical processes and structure of the composite with performance. We identified several swelling methods capable of attaining enhanced ionic conductivities per uptake compared to casting methods. Furthermore, each study demonstrated that optimization of the interface of the ionomer with other IPT components is essential to maximizing performance of novel IPTs beyond those constructed with Nafion®. Future work will concentrate upon isolation and confirmation of the effect of polymer architecture on IPT performance parameters such as uptake, hydrated modulus, and ionic conductivity as they perpetuate through the performance of the device.

CONCLUSIONS

The Army Research Office sponsored Multidisciplinary University Research Initiative (MURI) dealing with ionic liquids in electro-active devices has enabled the manufacture of electromechanical transducers in the presence of ionic liquids. Device fabrication using novel electrode deposition protocols has permitted the investigation of a wide range of polymer compositions. In addition, novel ionic liquid solvents and polymers derived from ionic liquid monomers has resulted in new families of ion-containing polymers and polyelectrolytes. Significant attention was devoted to the correlation of charged polymer composition on physical properties and ultimate performance. The team has addressed critical parameters for the construction of novel devices for emerging technologies.

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REFERENCES

- Amajjahe, S. and Ritter, H., 2008: Supramolecular Controlled Pseudo-LCST Effects of Cyclodextrin-Complexed Poly(ionic liquids), *Macromolecules*, **41**, 716-718.
- Ihm, J.E., and Cho, C.S. et al., 2005: Poly(4-vinylimidazole) as nonviral gene carriers: invitro and in vivo transfection, *Acta Biomaterialia*, **1**, 165-72.
- Overberger, C.G. and Vorcheimer., 1963: Imidazole-containing polymers. Synthesis and polymerization of the monomer 4(5)-vinylimidazole, *J. Amer. Chem. Soc.*, **85**, 951-955.
- Muldoon, M.J., and Charles, G.M., 2005: Synthesis of gel-type polymer beads from ionic liquid monomer, *J. Poly. Sci. A*, **42**, 3865-3869.